

Heavy Metal Concentrations in Ohio River Sediments—Longitudinal and Temporal Patterns¹

JOHN D. YOUNGER and WILLIAM J. MITSCH, Ohio Environmental Protection Agency, 1800 Watermark Drive, Columbus, OH 43266-1049, and School of Natural Resources, The Ohio State University, Columbus, OH 43210

ABSTRACT. Concentrations of barium, cadmium, chromium, copper, iron, lead, manganese, nickel, and zinc were determined in sediment samples collected in 1987 at 11 sites in the Ohio River between Pittsburgh, PA, and Louisville, KY. Samples were digested by nitric acid treatment. Concentrations of metals generally decreased with distance downstream, with highest values occurring in the industrial upper Ohio River. The longitudinal trend paralleled the pattern found 10 years earlier by the Ohio River Valley Water Sanitation Commission. Concentrations of cadmium, chromium, copper, iron, lead, nickel and zinc in 1987 were lower at most sites than those in 1977. In contrast, the manganese concentration was generally higher in 1987, while barium levels did not differ between the two sampling periods. Most metal concentrations in the Ohio River remain greater by two to eight standard deviations than background concentrations of metals published for the State of Ohio.

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INTRODUCTION

Even with the control of point and non-point sources of water pollution in our nation's rivers, sediments contaminated with metals and other pollutants may be pollution sources to overlying waters and benthic food chains for years to come (Lyman et al. 1987). Heavy metals from industrial and wastewater treatment plant effluents can form stable complexes with inorganic and organic compounds (Nienke and Lee 1982, Moore and Ramamoorthy 1984), settling where the average velocity is less than 0.2 m/sec (0.6 ft/sec). With time, these deposits may consolidate and stabilize, forming large deposits which require scour velocities as high as 0.35 m/sec (1.15 ft/sec) for removal (Velz 1970). Sediment deposits form precise records of industrial activity in a drainage basin and have been correlated to changes in regional economies (Thomas 1972, Aston et al. 1973, Christensen and Goetz 1987). Mathis and Cummings (1973) found that metal concentrations downstream of industrial sources were several times higher in the Illinois River than in non-industrial-use streams. Sediment records have also been used in forensic investigations to trace pollutants back to sources, to document compliance of dischargers with National Pollutant Discharge Elimination System (NPDES) permit limitations and to point to the need for permit changes (Meiggs 1980). These deposits represent large potential sources of heavy metals which may reenter the water column through stream scouring, anaerobic release, or bioaccumulation (Horowitz 1985, Gibbs 1973, Elder and Mattraw 1984). In addition, dredging of river sediments either for channel deepening or as a source of landfill can contaminate terrestrial environments.

Little is known about the concentration of heavy metals in Ohio River sediments or the possible improvement in the quality of river sediments over long periods after pollution sources are controlled or eliminated. In the past, significant metal contamination of Ohio River sediments resulted from a number of sources. Coal mine drainage leads to inflows of iron and manganese in the

upper Ohio River. Industrial activity, particularly the iron and steel industry of the upper Ohio River Valley, has also been a major contributor of certain metals to the water and sediments of the river. The Ohio River has experienced a significant decrease in pollution-causing industrial activity and there has been an active water pollution control strategy on the river by the Ohio River Valley Water Sanitation Commission (ORSANCO). While some improvement in the water quality of the Ohio River has been noted (e.g., Van Hassel et al. 1988, Cavanaugh and Mitsch 1989), further improvement may be hampered by the contamination in the river's sediments.

We report the concentrations of nine heavy metals (barium, cadmium, chromium, copper, iron, lead, manganese, nickel, and zinc) in Ohio River sediments collected in 1987 at eleven locations along a 1000 km reach of the river between Pittsburgh, PA and Louisville, KY. Longitudinal distribution and concentrations for the metals are compared to those measured by ORSANCO (unpublished data) one decade before. Concentrations are also compared with published background levels for the State of Ohio to estimate the significance of the concentrations in the Ohio River.

MATERIALS AND METHODS

Sediment samples were collected at 11 sites on the Ohio River (Figure 1) from 21 July to 1 August, 1987, during the research/educational voyage "Boatload of Knowledge" (Mitsch et al. 1989). The sampling sites extended from river miles (RM) 6.2 to 531.5 on the Ohio River with most located upstream of navigation locks. Only one of the sampling sites (RM 63) was immediately downstream of a known major discharger (Weirton Steel at RM 62.5).

Sediments were collected using a 20-cm stainless steel Eckman dredge. Because grain size is one of the most important factors determining metal concentration in sewerage sludge (Campbell et al. 1988) and sediments (Forstner and Salomons 1984, Horowitz and Elrick 1988), only fine grain silt/clay sediments were collected. These fine grain sediments were usually found within 100 m of the bank due to high sediment scour in the middle of the river. After collection, samples were transferred to glass jars, stored on ice in a cooler, and submitted to the Ohio Environmental Protection Agency Chemistry Laboratory (Ohio EPA) for analysis at the end of the two-week voyage. The sediment samples were held at room temperature until analysis, which occurred in about two months. A blind duplicate was submitted for RM 531 for quality assurance purposes.

The samples were prepared and analyzed according to Ohio EPA Method WQMA-AC-1 (Ohio EPA 1987). Each sample was passed

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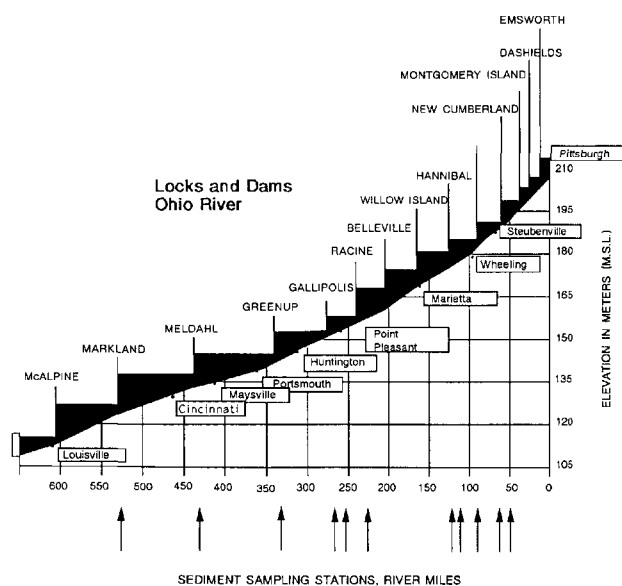


FIGURE 1. Arrows indicate location of sediment sampling sites on Ohio River relative to navigation dams and major urban areas. Numbers indicate river miles downstream of beginning of Ohio River at Pittsburgh, PA, and elevation in meters above mean sea level.

through a 2-mm plastic sieve. Two 10-gram cores were collected from the sieved material with a glass tube. One core was analyzed for metals and the other for percent moisture. Cores for metals analyses were subjected to several successive acid digestion treatments (Ohio EPA 1987). The procedure began with digestion of the sediment in concentrated HNO_3 and 30% H_2O_2 , followed by digestion with concentrated HCl and heating. Enough HNO_3 was added to make a 0.5% solution. Digestates were filtered through Whatman No. 40 filter paper, the residue on the filter paper was washed three times with distilled water, and the filtrate was collected in a flask. The collected filtrate was analyzed with a Perkin Elmer 5000 atomic absorption spectrophotometer according to procedures appropriate for the particular metal. The data on percent moisture were used to estimate the dry weights and the final concentrations of each metal as μg per g dry weight sediment. Quality control standards within the working range of the unknown values were analyzed like regular samples and laboratory duplicates, blanks, and spiked samples were run for every ten samples. Samples taken by ORSANCO in 1977 were analyzed by the U.S. Geological Survey Laboratory in Atlanta,

GA, using acid extraction techniques similar to those used by the Ohio EPA Laboratory for this study (Skougstad et al. 1979).

RESULTS AND DISCUSSION

Our 1987 metal concentrations and the 1977 ORSANCO concentrations are presented in Table 1. The quality assurance (duplicate) samples are shown as paired values (a and b) for river mile 531. Differences were usually slight ($<7\%$) except for a difference of 14% for the cadmium concentrations. Overall, concentrations were ranked, from greatest to lowest, as follows:

$\text{Fe} > \text{Mn} > \text{Zn} > \text{Ba} > \text{Pb} > \text{Ni} > \text{Cr} > \text{Cu} > \text{Cd}$

Longitudinal Patterns

Concentrations of most metals were highest below cities with heavy industrial activity, particularly in the Upper Ohio River (upstream of Hannibal lock and dam, RM 126) and generally decreased with distance downstream toward Louisville. The concentrations of barium, cadmium, copper, manganese, and nickel were highest in the lock pools immediately downstream of East Liverpool, OH (RM 54) and the Wheeling, WV metropolitan area (RM 118 and 126). Concentrations of barium were also high below the Ashland (KY)-Huntington (WV) area (RM 340) and manganese increased again below Point Pleasant (WV)-Gallipolis (OH) (RM 279). The concentration for chromium was highest in the lock pool below Steubenville, OH (RM 83), in the heavily industrialized Upper Ohio River Valley. There was usually a slight upturn in concentration of all metals, except for cadmium and zinc, at RM 531. We believe that this is a real phenomenon and illustrates the effects of present and past discharges from the Cincinnati metropolitan area, which are generally located between the confluences of the Ohio River with the Little Miami River (RM 463) and the Greater Miami River (RM 491).

Comparison with 1977 Data

Table 1 also compares average concentrations from our 1987 study with data of Ohio River sediments from

TABLE 1.

Metals concentrations in sediments at Ohio River sampling sites in 1977 (ORSANCO, unpub. data) and in 1987 (this study). Concentrations are in $\mu\text{g/g}$ dry weight of sediment, except for iron and manganese, which are in mg/g dry weight of sediment.

River Mile	Barium		Cadmium		Chromium		Copper		Iron (mg/g)		Lead		Mn (mg/g)		Nickel		Zinc	
	1977	1987	1977	1987	1977	1987	1977	1987	1977	1987	1977	1987	1977	1987	1977	1987	1977	1987
6.2	150	—	5	—	86	—	100	—	70	—	200	—	1.4	—	100	—	900	—
54	—	186	—	2.02	—	34.3	—	54.0	—	35.3	—	80.0	—	2.89	—	83.5	—	465
63	—	105	—	1.15	—	74.5	—	36.8	—	27.8	—	77.3	—	1.56	—	53.0	—	728
83	98	101	3	1.32	110	130	69	58.5	58	37.8	180	75.8	1.1	1.38	90	58.5	700	491
118	—	157	—	1.45	—	40.0	—	40.0	—	37.0	—	71.3	—	1.2	—	42.0	—	440
126	—	189	—	2.16	—	48.9	—	62.5	—	39.0	—	74.8	—	2.61	—	91.4	—	634
161	140	—	3	—	76	—	63	—	47	—	130	—	1.0	—	89	—	340	—
237	—	113	—	0.837	—	32.6	—	28.2	—	29.3	—	38.8	—	1.41	—	46.6	—	263
265	—	96.5	—	0.473	—	12.6	—	29.5	—	22.3	—	29.9	—	0.85	—	29.4	—	158
279	160	127	1	0.96	36	31.2	45	34.4	29	27.0	49	51.0	1.2	1.91	51	48.4	270	252
340	31	178	<1	0.884	6	25.3	7	34.0	10	25.8	8	44.8	0.29	1.04	20	38.2	47	235
435	130	115	2	0.855	54	23.7	51	27.1	35	21.2	79	31.8	1.4	0.96	59	34.5	370	207
531a	—	143	—	0.792	—	24.3	—	35.3	—	25.5	—	35.4	—	1.48	—	40.6	—	188
531b	—	139	—	0.907	—	24.2	—	36.2	—	24.6	—	37.8	—	1.43	—	40.9	—	193
Ave	118	137	2.5	1.2	61.3	43.4	55.8	40.1	41.5	29.8	107.7	55.6	1.1	1.57	68.2	51.5	438	369
Std Dev	19	11	0.6	0.1	15.2	9.9	12.5	3.8	8.8	1.9	30.8	6.1	0.2	0.2	12.4	5.9	126	58

10 years before. While the averages can be misleading because they were not obtained from the same sites and because of the unequal sample size, lower concentrations occur in 1987 for all of the metals except barium and manganese.

When the data were compared in paired fashion for three sites which were sampled in both 1977 and 1987, the latter values were generally lower for all metals studied except manganese. Manganese increased slightly in concentration between 1977 and 1987 but the difference is not significant. Concentrations reported for RM 340 by ORSANCO in the 1977 data were not used in this comparison because the values were consistently lower than those reported for other sites by wide margins, suggesting inadequate analyses, improper moisture calculations, or a sediment sample with different texture and sorption capacity. Using a paired t-test, only cadmium and copper are significantly lower in 1987 at $P \leq 0.1$ level of significance and iron, nickel, and zinc at $P \leq 0.2$ level. All of these metals are associated with the iron and steel industry, which experienced a dramatic decrease in activity during the 1977-87 decade in the upper Ohio River valley.

The "improvement" in sediment quality from 1977 to 1987 mirrors some of the change that has occurred in the water quality. Cavanaugh and Mitsch (1989) found through trend analysis of the upper Ohio River that there was some improvement in water quality over the 1977 to 1987 decade. The metals that were examined in that study showed moderate decreases in water concentrations of lead and zinc and minor decreases in copper. It appears that there was improvement in both the water quality and the sediments of the Ohio River over this decade. Improvement in water quality is predictable when discharges are controlled; however, improvement in sediment quality would not necessarily occur in such a short period of time due to their longer retention time. Both sets of data, along with data on increased populations and numbers of pollution-intolerant species of fish from 1973 to 1985 (Van Hassel et al. 1988), indicate a cleaner Ohio River.

Comparison with Background Values

A "cleaner" Ohio River must be evaluated in absolute as well as relative terms. The present data were compared with groupings developed by Heitzman (1987), as modified from Kelly and Hite (1984), to determine the significance of the concentrations of sediment metals found in the Ohio River. The number of sites where the 1987 samples were classified as "non-elevated" (no difference), "slightly elevated" (greater by one standard deviation), "elevated" (greater by two standard deviations), "highly elevated" (greater by four standard deviations), and "extremely elevated" (greater by eight standard deviations) compared to background sediment data for the state of Ohio have been determined (Figure 2). Although concentrations of many of the metals have decreased over the past decade, absolute values of seven of the metal concentrations remain high. Concentrations of chromium, copper, and zinc are highly to extremely elevated at most of the sampling sites, indicating that concentrations of these metals were generally at least four standard deviations greater than "background" concentrations

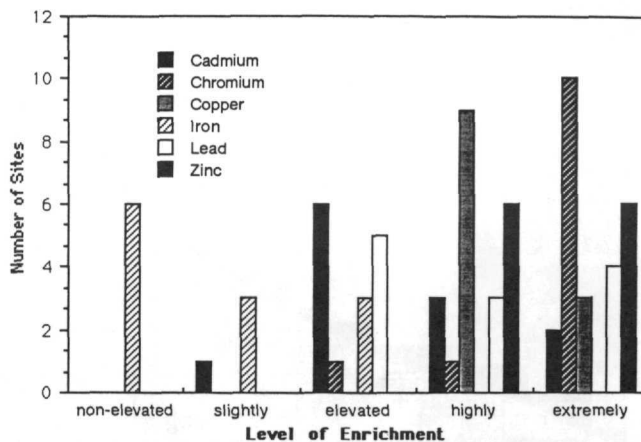


FIGURE 2. Metal concentrations in Ohio River sediments (1987 data) relative to background concentrations of metals in Ohio sediments as defined by Heitzman (1987) for cadmium, chromium, copper, iron, lead, and zinc. Frequency refers to the number of sites in each enrichment classification. Slightly elevated is greater than background by one standard deviation, elevated by two standard deviations, highly elevated by four standard deviations, and extremely elevated by eight standard deviations. Non-elevated concentrations are less than one standard deviation greater than background.

typical of uncontaminated Ohio streams and rivers. Chromium and zinc were "extremely elevated", or at least eight standard deviations above background at all of the sampling sites upstream of RM 265 on the Ohio River. Cadmium and lead were usually greater than background by at least two standard deviations. Iron concentrations were generally the closest to background (19.3 ± 8.8 mg/g) with six of eleven sites showing no difference from background (within one standard deviation).

The present data indicate some reductions in the concentrations of metals in the Ohio River over the 1977-87 decade and a continuing pattern of decreasing concentrations as one proceeds downstream from the heavily industrial upper Ohio River. Concentrations generally remain well above background and therefore may be a source of water contamination in the Ohio River for some years to come.

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